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13. ABSTRACT *(Maximum 200 words)*

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Intrinsic fluorescence from DDS is used by correlating the red spectral shifts in excitation spectra with the extent of cure. This spectral shift is due to the reaction of DDS amine with epoxide which converts primary amine groups to tertiary amine groups. The technique is applied to neat epoxy cured with DDS as well as composite prepegs reinforced with fibers, using a fiber-optic fluorimeter, and taking into account the effects of temperature on the spectral shift.

Use of the fluorescence technique to monitor water uptake is explored, by adding a small amount of extrinsic fluorophore, or by investigating the intrinsic fluorescence near 460 nm in cured epoxy which is probably due to side reaction products. As the water is absorbed, the fluorescence intensity decreases, allowing small amounts of water to be detected.

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Fluorescence characterization of cure and water uptake in polymers and composites

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Abstract

This paper summarizes our recent research on using intrinsic fluorescence for cure characterization, and extrinsic and intrinsic fluorescence approaches for monitoring water uptake in epoxy cured with a widely used aromatic diamine curing agent (diaminodiphenyl sulfone, DDS).

Intrinsic fluorescence from DDS is used by correlating the red spectral shifts in excitation spectra with the extent of cure. This spectral shift is due to the reaction of DDS amine with epoxide which converts primary amine groups to tertiary amine groups. The technique is applied to neat epoxy cured with DDS as well as composite prepregs reinforced with fibers, using a fiber-optic fluorimeter, and taking into account the effects of temperature on the spectral shift.

Use of the fluorescence technique to monitor water uptake is explored, by adding a small amount of extrinsic fluorophore, or by investigating the intrinsic fluorescence near 460 nm in cured epoxy which is probably due to side reaction products. As the water is absorbed, the fluorescence intensity decreases, allowing small amounts of water to be detected.

1. Introduction

Higher performance composites using an organic resin matrix reinforced with fibers are being increasingly used as structural parts in many applications. Characterization of the extent of cure and water-uptake in polymers and composites before, during and after the manufacturing process is extremely important for reproducible processability and achievement of consistent mechanical properties.

While microdielectrometry [1] and fiber-optic Fourier transform (FT) IR spectroscopy [2] have been reported for *in situ* cure monitoring, during the last eight years our research has focused on the development of fluorescence and UV-visible techniques. As a first approach, we used a reactive label as an extrinsic fluorophoric sensor. This approach is different from viscosity-sensitive fluorescent probes which do not react with the polymer systems [3]. We first applied this technique to epoxy cured with diaminodiphenyl sulfone (DDS) which forms a matrix resin for composites, and *p,p'*-diaminoazobenzene (DAA) revealed a sensitive enhancement of fluorescence intensity due to the much greater quantum yield of tertiary amines of DAA as a result of reaction with epoxide [4]. Recently, this extrinsic cure sensor (DAA) has been used for *in situ* cure monitoring of bulk epoxy cured with DDS at high cure temperatures (140–180 °C) using a fiber-optic fluorescence instrument [5]. However, when using the DAA extrinsic sensor, an internal standard dye is necessary to correct for external factors which affect the fluorescence intensity. For *in situ* monitoring at high cure temperatures, the temperature dependence of the fluorescence intensity has been evaluated and this provides a basis for reducing the DAA fluorescence intensity to any reference temperature and correlating it to the extent of cure.

More recently, we found that the intrinsic fluorescence signal from the DDS curing agent is sensitive to the extent of cure. We first describe our study of intrinsic fluorescence for cure characterization in neat epoxy–DDS [6] and its application to glass or graphite reinforced epoxy composites [7].

The second part of this paper will deal with our recent attempt to explore fluorescence techniques for measuring water uptake in the epoxy-DDS system [8]. Even a small amount of water uptake in polymers and composites can influence their properties by decreasing the glass transition temperature and thus reducing their modulus. While several other techniques such as

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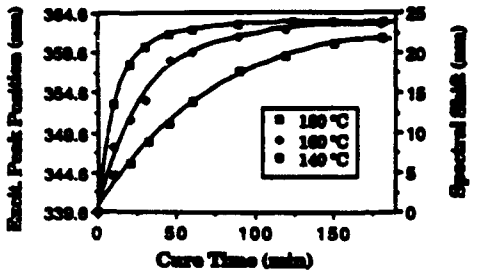


Fig. 2. Changes in the excitation peak positions as a function of cure time at three temperatures for DGEB-DDS epoxy.

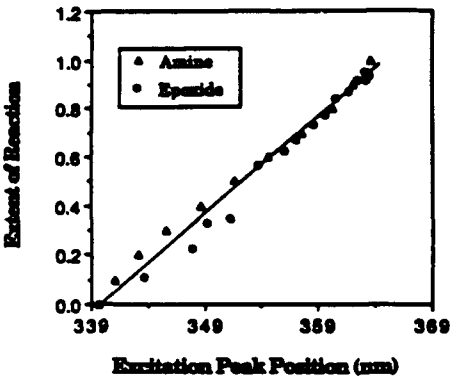


Fig. 3. Correlation between the extent of amine reaction or the extent of epoxide reaction and the excitation peak position.

at three different curing temperatures (140, 160 and 180 °C).

In order to see how the fluorescence excitation peak position can be correlated with the extent of amine reaction, the excitation spectra of DGEB-DDS epoxy at different extents of cure were simulated based on the amine-addition kinetics of epoxide described by Dusek and Bleha [13]. As expected, the spectral maximum is shifted to a longer wavelength as the extent of amine reaction increases. A linear correlation between the excitation peak position and the extent of amine reaction was obtained, as shown in Fig. 3. Furthermore, we measured the extent of the epoxide reaction of DGEB-DDS as a function of curing time at 160 °C by FTIR. As shown in Fig. 3, the excitation peak position of DGEB-DDS epoxy can also be linearly correlated with the extent of epoxide reaction. This result confirms that the amine-addition reactions are the major reactions for the DGEB-DDS epoxy.

In order to insure that these shifts in spectra are due to cure reactions and not to changes in the matrix (*e.g.* polarity change during cure), fluorescence emission and excitation spectra of a fully substituted DDS (*t,t*-DDS) in the stoichiometric mixture of DDS and EDDA (ethylene dioxyl diethyl amine) were obtained before and after 1 h cure at 120 °C. EDDA is an aliphatic diamine with no absorbance in the UV spectral region of interest. In this case, any spectral change would be due to the matrix effect since *t,t*-DDS cannot react further with the epoxide. In fact, only negligible blue shifts (less than 3 nm) were observed. The blue shifts are probably caused by the decreasing matrix polarity after cure, as observed by measurement of the dielectric constant of epoxy resins [14]. Therefore, we can deduce that the spectral shifts obtained in the emission and excitation spectra of DDS epoxy arise from cure reactions.

For DGEBA-DDS, the total red shift observed in the excitation spectra was 17 nm when cured at 160 °C. This lower extent of amine reaction is due to the vitrification and quenching of the cure at 160 °C which is below the maximum T_g value of the fully cured DGEBA-DDS.

For TGDDM-DDS, the emission spectra are very broad ranging from 360 to 465 nm. Moreover, the emission from DDS is overlapped by another strong emission peak at about 465 nm, probably owing to the presence of some fluorescent impurities, oxidation or degradation products during cure. Excitation spectra of the stoichiometric TGDDM-DDS system were obtained by emitting at 410 nm. When cured at 160 °C, a total red shift of about 20 nm was obtained from stoichiometric TGDDM-DDS epoxy, which is larger than that of the stoichiometric DGEBA-DDS system (17 nm).

In summary, the intrinsic fluorescence of DDS curing agent was found to exhibit significant bathochromic shifts in emission and excitation spectra during cure with either a diepoxide or a tetraepoxide. The spectral shifts correlate well with the extent of cure of the epoxies. Since no extrinsic fluorophore is required, this technique can be used for *in situ* cure monitoring in composites with a fiber-optic instrument.

3.2. Cure monitoring using a fiber-optic instrument

Fluorescence excitation spectra of a stoichiometric mixture of DGEBA-DDS in a test tube were obtained using a fiber-optic fluorimeter by emitting at 420 nm. Figure 4 shows a series of excitation spectra obtained as a function of cure time at 140 °C. These spectra represent difference spectra since the fiber background was subtracted. As curing proceeds, the excitation peak shifts to a longer wavelength as a result of conversion of primary amine to secondary and tertiary amines. The peak positions in this study are about 15 nm higher than those observed at room temperature in a conventional fluorescence instrument [6]. This discrepancy may be due to the different wavelength calibration in both instruments as well as to some temperature dependence of the excitation maxima. However, the overall spectral shift during cure is very

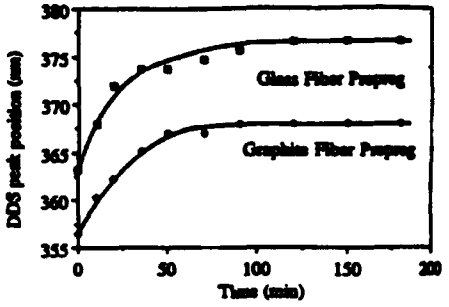
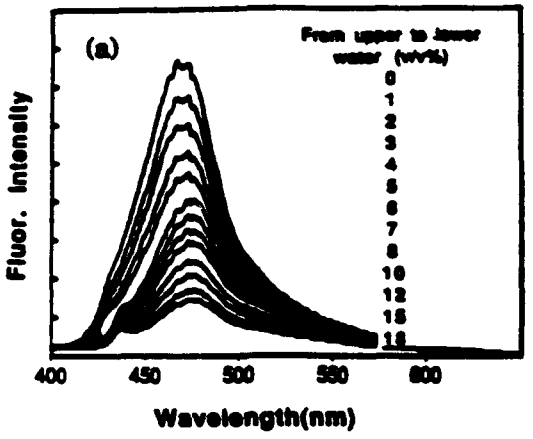


Fig. 8. DDS excitation peak position during cure at 180 °C in glass and graphite fiber prepregs (TGDDM-DDS).



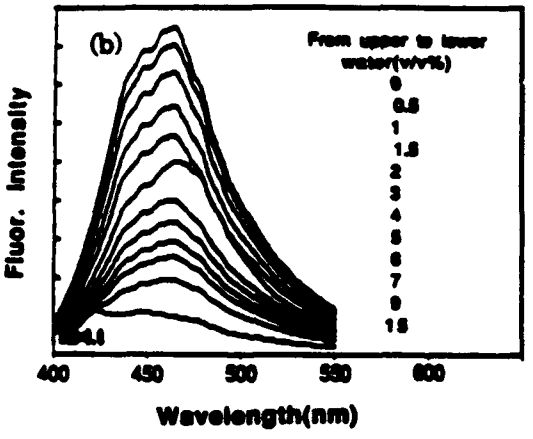
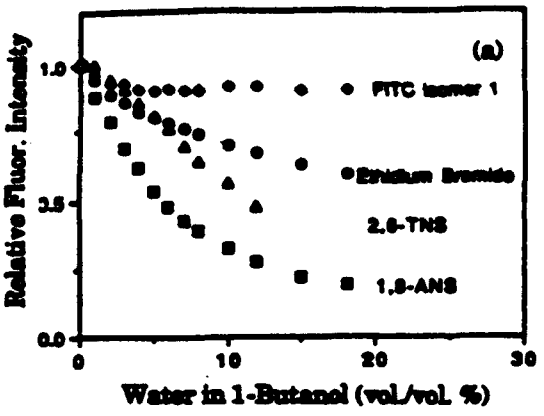


Fig. 9. Fluorescence spectra of (a) 1,8-ANS in 1-butanol and (b) 9-AA in NMP as a function of added water.



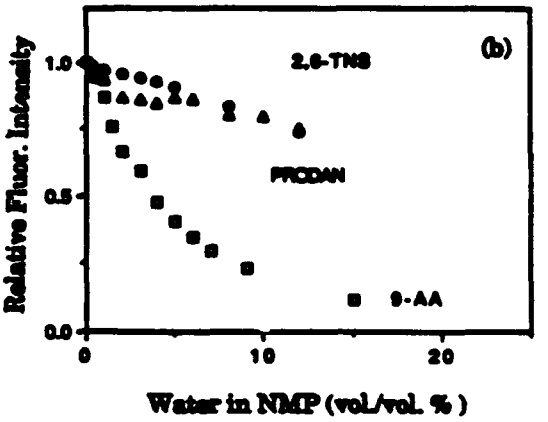


Fig. 10. Changes in fluorescence intensity as a function of added water either in 1-butanol (a) or NMP (b) for seven extrinsic fluorophores.

epoxy. Possible explanations for these findings are under investigation. It is clear, however, that the fluorescence technique is an effective tool for monitoring autoclave curing during the composite manufacturing process.

3.3. *Water uptake monitoring*

Figures 9(a) and 9(b) show the changes in fluorescence emission spectra when excited at 385 nm for 1,8-ANS in 1-butanol and 9-AA in NMP as a function of water content respectively. A large decrease in intensity is observed while only a small spectral red shift is observed, owing to the fact that 1-butanol and NMP are polar solvents. Figure 10 illustrates the decrease in intensity for seven extrinsic fluorophores tested. Of these, 1,8-ANS and 9-AA showed the most sensitive behavior, by losing 80%–90% intensity when the water content was about 15–18 vol./vol.%. In 1,8-ANS, the intensity decrease could be due to lowering of the S_1 state and the subsequent ease of intersystem crossing, since the energy difference between S_1 and T_1 states is relatively small [16]. For the excited 9-AA molecule, carbonyl oxygen can form an intramolecular hydrogen bond which is disrupted when water is added, leading to increase in internal conversions [17].

Figure 11 shows the fluorescence spectra of DDS-DGEB epoxy without any extrinsic fluorophore as a function of cure time at 160 °C, when excited at 385 nm. This intrinsic fluorescence which initially increases with cure time may be due to the oxidation and/or degradation products formed during cure. When immersed in water at 20 °C, this intrinsic fluo-

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